Site-Competition Epitaxy for Controlled Doping of CVD Silicon Carbide

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ABSTRACT: A "site-competition" epitaxy technique based on the use of the Si/C ratio for dopant control is presented for silicon carbide CVD epitaxial layers. This technique is also applicable to the general growth of silicon carbide. Results from room temperature mercury-probe CV and low temperature photoluminescence (LTPL) measurements indicate that very low net carrier concentrations of about 1×10^{14} cm^{-3} are achievable using this novel growth technique. This growth technique also affords intermediate dopant control as well as the production of degenerately doped n-type and p-type epilayers, estimated to be $>1 \times 10^{19}$ cm^{-3}, which result in "ohmic as deposited" contacts for a variety of metals. Superior electronic devices have also been accomplished using site-competition epitaxy, including world-record breaking 3C- (>200 V) and 6H- (>2000 V) silicon carbide diodes.

1. INTRODUCTION

The success of silicon carbide (SiC) for high temperature and high power electronic applications is dependent upon the ability to reproducibly attain high quality SiC epilayers. This includes the ability to produce, in situ, both n-type and p-type epilayers with doping profiles ranging from extremely low doped epilayers for high voltage devices to degenerately doped layers for minimizing parasitic resistances. In the past, the reproducible doping range for SiC epilayers has been typically limited to net carrier concentrations ranging from n $=2 \times 10^{16}$ cm^{-3} to 5×10^{18} cm^{-3} for n-type and from n $= 2 \times 10^{16}$ cm^{-3} to 1×10^{18} cm^{-3} for p-type epilayers (Cree 1991, Clemen et al 1992). Removing these lower doping limitations would ultimately allow the fabrication of devices with larger blocking voltages whereas the availability of higher doped epilayers would aide in minimizing parasitic resistances in SiC electronic devices, especially contact resistances. These improvements would enable large advancements in the performance and capabilities of SiC electronic devices.

We have discovered and now report on an epilayer growth process (Larkin et al, 1992) which serves to expand the doping capabilities in SiC epilayer growth. Aspects of this work were previously reported in the form of electrical characterization of 3C-SiC and 6H-SiC high voltage devices (Neudeck et al 1993a, 1993b). Our experimental data supports a proposed mechanism for this growth technique, called "site-competition epitaxy", which allows a greater latitude in the control of dopant levels and doping profiles in CVD SiC epilayers.

2. EXPERIMENTAL, RESULTS, AND DISCUSSION

The 3C-SiC and 6H-SiC epilayers were grown at 1450°C on commercially available (Cree) n+ 6H (0001) silicon-face SiC substrates with tilt angles ranging from 0.2° to 0.6° and 3° to 4°, respectively.   The SiC substrates were placed onto an SiC-coated graphite susceptor and loaded into a water-cooled quartz reactor CVD system, as described previously by Powell et al. (1987). The grown SiC epilayers were routinely examined using mercury-probe or pn diode CV to determine active doping concentrations.

We have discovered and report for the first time that the Si/C ratio within the growth reactor has a strong influence on intentional and unintentional dopant incorporation of the growing 6H, 3C, and 4H SiC(0001) epilayers. We report here on the results obtained from growth on the 6H-SiC(0001) Si-face only, because the growth on the C-face is still under investigation. Specifically, the active n-type (nitrogen) carrier concentration was found to be directly proportional to the Si/C ratio, whereas, the active p-type (aluminum) concentration was found to be inversely proportional to the Si/C ratio for epilayer growth on the SiC(0001) basal plane. For example, as the Si/C ratio within the growth reactor was decreased, the active nitrogen concentration in the grown SiC epilayer decreased. When the Si/C ratio was decreased further to Si/C $\approx$ 0.1, the unintentionally doped epilayers changed from n-type to p-type.   As a result, we have obtained both p-type and n-type epilayers with room temperature carrier concentrations of 1×10^{14} cm^{-3}, as measured by both mercury-probed CV and low temperature photoluminescence (LTPL) (Yoganathan et al. 1993). Previously, the unintentionally doped epilayers produced in our lab were exclusively n-type with the lowest net carrier concentrations typically limited to about n = 2×10^{16} cm^{-3}.

Dopants in SiC are believed to occupy specific sites, specifically nitrogen occupies the carbon site while aluminum occupies the silicon site of the SiC lattice (Choyke 1990, Davis and Glass 1991b).   Based upon this information, and on our experimental results of decreasing the Si/C ratio, we propose that the relative increase in carbon concentration "outcompetes" the nitrogen for the C-sites of the growing SiC lattice. The analogous situation exists for an increased Si/C ratio, in which the relative increase in silicon concentration "outcompetes" the Al for the Si-sites of the growing SiC lattice. We refer to this model as "site-competition" epitaxy and use it to rationalize the experimental results of active dopant dependence on the Si/C ratio. We have completed numerous experiments which support this model. For example, we have introduced 100 ppm of N (50 ppm N$_2$) into our growth reactor and then attempted to exclude it from the growing epilayer by only decreasing the Si/C ratio from about Si/C = 0.44 to Si/C = 0.1. The Si/C of 0.1 results in consistently producing an intentionally doped n-type SiC epilayer with a net carrier concentration of n = 1×10^{15} cm^{-3}. In contrast, growth using the more typical Si/C = 0.44 with 100 ppm of N results in n-type epilayers of n = $1-2 \times 10^{17}$ cm^{-3}. For epilayer growth using the Si/C ratio of 0.1, the increased amount of carbon is believed to have outcompeted the nitrogen for the C-sites of the growing SiC lattice.

Further corroborating evidence to support this model was obtained in producing p-type epilayers. For these series of experiments a flow of TMA was introduced into the reactor during epilayer growth. The resulting p-type epilayer grown with a Si/C ratio of 0.44 was measured to be 5×10^{16} cm^{-3}, while the epilayer grown using a Si/C ratio of 0.1 yielded a degenerately doped p-type epilayer with an estimated net carrier concentration of 1×10^{19} cm^{-3}.

These experimental results support the hypothesis that as the Si/C ratio is decreased from 0.44 to 0.1, the relative amount of Si competing with the Al for the Si-sites of the SiC lattice also decreases, which results in an increased Al incorporation.

Site-competition epitaxy was also successfully used to obtain very abrupt changes in dopant concentrations in SiC epilayers. In conventional CVD systems, the abruptness of the dopant profile is limited by the purging of the dopant-source from the growth reactor. One advantage of epilayer growth using site-competition epitaxy is that more abrupt dopant profiles can be obtained by excluding the remaining unwanted dopant by changing the Si/C ratio along with the dopant-source gas. Conversely, very abrupt, enhanced dopant incorporation can be accomplished for production of highly degenerately doped epilayers. One highly useful example of this is our ability to form very thin degenerately doped p-type and n-type contact layers by ceasing the source-flow of Si or C, respectively, during the last minutes of epilayer growth. Subsequently deposited metal contacts are "ohmic as deposited" for a wide variety of metals on both p-type and n-type epilayers. Some preliminary contact resistivities determined for as-deposited molybdenum on both n-type and p-type degenerately doped epilayers were calculated to be $\rho_c < 5E{-}5$ Ω cm^2 using the linear TLM method (Petit et al. 1993a, 1993b).

Preliminary Hall measurements on intentionally doped 6H-SiC epilayer samples have been carried out. N-type epilayers with $n = 8\times10^{16}$ cm^{-3} were found to be less than 10% compensated with room temperature Hall mobilities ranging from 247 to 253 cm^2/V-s. At room temperature, the heavily doped n-type contact epilayers yielded mobilities near 60 cm^2/V-s and measured low-electric-field free carrier concentrations of $n = 4\times10^{18}$ cm^{-3}. When incomplete ionization is taken into account (Ghezzo 1992), the 4×10^{18} cm^{-3} low-field free carrier concentration theoretically translates into atomic nitrogen concentrations in excess of 2×10^{19} cm^{-3}. The "ohmic-as-deposited" state of the contacts precluded conventional C-V profiling of the heavily doped epilayers. It is believed that the higher electric fields exerted by the C-V technique (relative to the Hall technique) should lead to higher measured free carrier concentrations because of field-enhanced ionization that would take place within the high-field depletion region of a Schottky diode (Gautier et al. 1991).

For the lowest doped n-type and p-type epilayers, low temperature photoluminescence (LTPL) was employed to determine crystalline perfection and relative dopant incorporation. Pensl and Choyke (1993) have recently correlated dopant concentration with I_{77}/P_o and I_{77}/S_o peak-height ratios for low-doped SiC, where P_o and S_o are the nitrogen donor no phonon lines at 3.00 eV and at 2.99 eV, respectively, and I_{77} is the SiC intrinsic peak intensity at 2.947 eV. The I_{77}/P_o intensity ratio increases as both the crystalline perfection increases and the dopant incorporation decreases in the SiC epilayer. The LTPL results from our lowest unintentionally doped p-type epilayer resulted in a $I_{77}/P_o = 150$ and an $I_{77}/S_o = 4.7$, which is the most intrinsic SiC reported to date (Choyke 1993). The estimate of unintentional dopant concentration by LTPL (1×10^{14} cm^{-3}) is consistent with our mercury-probe CV room temperature measurements of $p < 5\times10^{14}$ cm^{-3}. These results are more consistent with the site-competition model and do not support a more simplistic model of dopant compensation.

Superior electronic devices have been achieved using site-competition epitaxy. Among these, which have been presented elsewhere (Neudeck, et al. 1993a, 1993b) and also at this

conference (Neudeck, et al. 1993c), are high voltage 6H-SiC diodes (2000 V) and 3C-SiC diodes (200 V) which exhibit the largest SiC blocking voltages reported to date.

3. SUMMARY

A novel growth method, based on the use of appropriate Si/C ratios during epilayer growth to affect control over dopant concentration, has been demonstrated for SiC(0001) basal plane 6H- and 3C-SiC. We propose a model, called site-competition epitaxy, which is based on this method and is consistent with our experimental observations of active carrier concentration change as the Si/C ratio is varied from about 0.1 to 0.8. The donor carrier concentration in the grown epilayer is proportional to the Si/C ratio whereas the acceptor carrier concentration is inversely proportional to the Si/C ratio. The resulting surface morphologies and crystal quality were determined to be excellent for all Si/C ratios between 0.1 to 0.8. Results from both LTPL and CV measurements suggest that the active dopant concentration can be controlled by using the appropriate Si/C ratio. This growth method was used to produce very low-doped epilayers for 6H-SiC and 3C-SiC diodes which exhibit record blocking voltages of 2000 V and 200 V, respectively, and also degenerately doped epilayers which result in "ohmic as-deposited" contacts for a variety of metals on both p-type and n-type SiC epilayers. Work is continuing in order to both fully utilize this growth technique and also to further elucidate the growth mechanism of site-competition epitaxy.

4. ACKNOWLEDGMENTS

5. REFERENCES

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